Claims

1. A process for the preparation of a grafted thermoplastic or elastomeric polymer or copolymer, which process comprises in a first step

A) the preparation of a nitroxyl terminated oligomer or polymer by controlled free radical polymerization of an ethylenically unsaturated monomer

a1) in the presence of a nitroxyl ether R'R"N-O-X wherein X is selected such, that cleavage of the O-X bond occurs and a radical X• is formed capable of initiating polymerization; or

a2) in the presence of a nitroxyl radical R'R"N-O• and a free radical initiator capable of initiating polymerization; and in a second step

B) heating, mixing and reacting the nitroxyl terminated oligomer or polymer of step A) together with a thermoplastic or elastomeric polymer or copolymer at a temperature of between 120° C and 300° C.

2. A process according to claim 1 wherein the thermoplastic or elastomeric polymer or copolymer is selected from the group consisting of a polyolefin and its copolymers, polystyrene and its block or graft copolymers, polymers and copolymers derived from 1,3-dienes.

3. A process according to claim 2 wherein the thermoplastic or elastomeric polymer or copolymer is selected from the group consisiting of

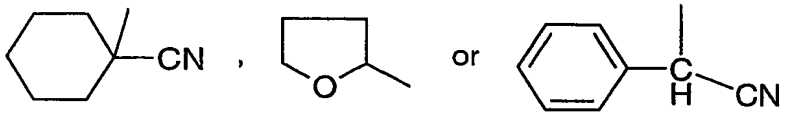
low density polyethylene (LDPE, LLDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), styrene-block copolymers (SI(S), SI, SB(S), ABS, ASA), ethylene-propylene-diene modified rubber (EPDM, EPM) and ethylene propylene rubber (EPR), polybutylene (PB), polyisobutylene (PIB), poly-4-methylpentene-1 (PMP).

4. A process according to claim 1 wherein the thermoplastic or elastomeric polymer or copolymer contains unsaturated bonds.

5. A process according to claim 1 wherein X is selected from the group consisting of

-CH_2-aryl, alkyl(C_1-C_{18})—CH(H)—aryl, -CH_2-CH_2-aryl, alkyl(C_1-C_{18})—C(H_3C)—aryl, (C_5-C_6cycloalkyl)$_2$CCN, (C_1-C_{12}alkyl)$_2$CCN, -$CH_2CH=CH_2$, (C_1-C_{12})alkyl-CR_{20}-C(O)-(C_1-C_{12})alkyl, (C_1-C_{12})alkyl-CR_{20}-C(O)-(C_6-C_{10})aryl, (C_1-C_{12})alkyl-CR_{20}-C(O)-(C_1-C_{12})alkoxy, (C_1-C_{12})alkyl-CR_{20}-C(O)-phenoxy, (C_1-C_{12})alkyl-CR_{20}-C(O)-N-di(C_1-C_{12})alkyl, (C_1-C_{12})alkyl-CR_{20}-CO-NH(C_1-C_{12})alkyl, (C_1-C_{12})alkyl-CR_{20}-CO-NH_2, -$CH_2CH=CH-CH_3$, -CH_2-$C(CH_3)=CH_2$,

-CH_2-CH=CH-phenyl, -CH_2-C≡CH, 3-cyclohexenyl, 3-cyclopentenyl,



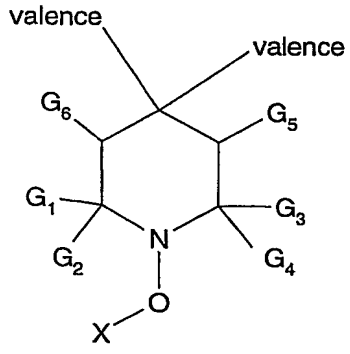
, wherein

R_{20} is hydrogen or C_1-C_{12}alkyl;

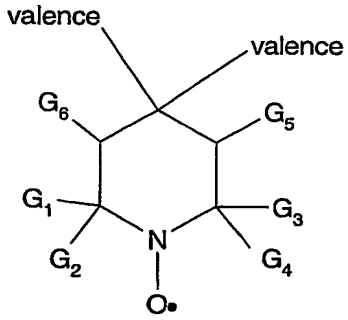
the alkyl groups are unsubstituted or substituted with one or more -OH, -COOH or –C(O)R_{20} groups; and

the aryl groups are phenyl or naphthyl which are unsubstituted or substituted with C_1-C_{12}alkyl, halogen, C_1-C_{12}alkoxy, C_1-C_{12}alkylcarbonyl, glycidyloxy, OH, -COOH or -COO(C_1-C_{12})alkyl.

6. A process according to claim 1 wherein the nitroxyl-ether or the nitroxyl radical contains a structural element of formula (Ia) or (Ib)



(Ia),

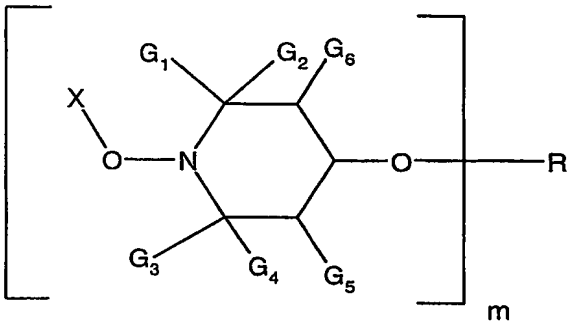


(Ib) wherein

G_1, G_2, G_3, G_4 are independently C_1-C_6alkyl or G_1 and G_2 or G_3 and G_4, or G_1 and G_2 and G_3 and G_4 together form a C_5-C_{12}cycloalkyl group;

G_5, G_6 independently are H, C_1-C_{18}alkyl, phenyl, naphthyl or a group $COOC_1$-C_{18}alkyl.

7. A process according to claim 6 wherein component a1) and a2) are of formula A, A', B, B' or O, O'



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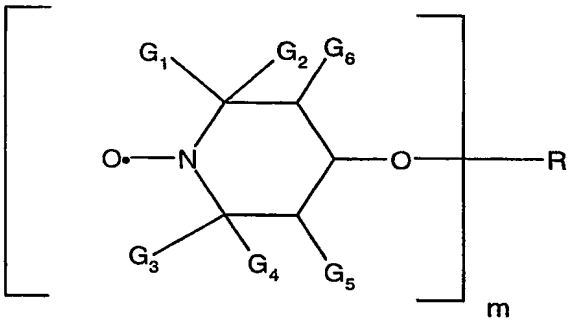

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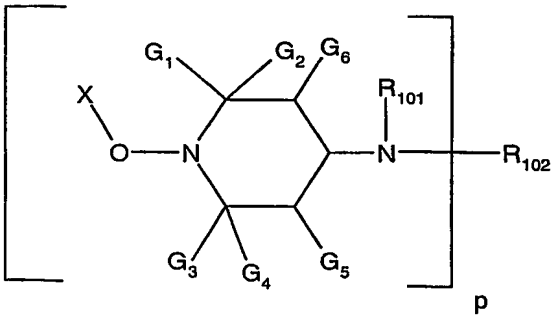

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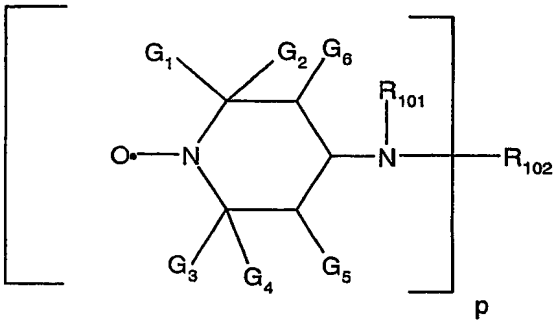

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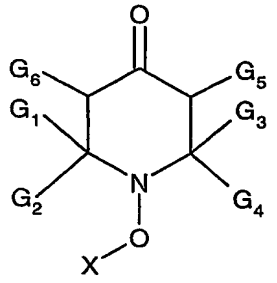

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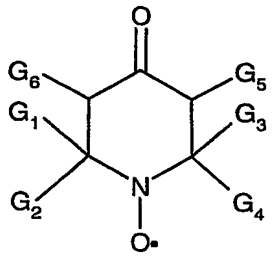


(O') ,

wherein

G_1, G_2, G_3 and G_4 are independently alkyl of 1 to 4 carbon atoms, or G_1 and G_2 together and G_3 and G_4 together, or G_1 and G_2 together or G_3 and G_4 together are pentamethylene;

G_5 and G_6 are independently hydrogen or C_1-C_4 alkyl;

m is 1, 2, 3 or 4

R, if m is 1, is hydrogen, C_1-C_{18}alkyl which is uninterrupted or C_2-C_{18}alkyl which is interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms, where each carboxylic acid can be substituted in the aliphatic, cycloaliphatic or aromatic moiety by 1 to 3 -$COOZ_{12}$ groups, in which Z_{12} is H, C_1-C_{20}alkyl, C_3-C_{12}alkenyl, C_5-C_7cycloalkyl, phenyl or benzyl; or

R is a monovalent radical of a carbamic acid or phosphorus-containing acid or a monovalent silyl radical;

R, if m is 2, is C_2-C_{12}alkylene, C_4-C_{12}alkenylene, xylylene, a divalent radical of an aliphatic dicarboxylic acid having 2 to 36 carbon atoms, or a cycloaliphatic or aromatic dicarboxylic acid having 8-14 carbon atoms or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8-14 carbon atoms, where each dicarboxylic acid may be substituted in the aliphatic, cycloaliphatic or aromatic moiety by one or two -$COOZ_{12}$ groups; or

R is a divalent radical of a phosphorus-containing acid or a divalent silyl radical;

R, if m is 3, is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, which may be substituted in the aliphatic, cycloaliphatic or aromatic moiety by -$COOZ_{12}$, of an aromatic tricarbamic acid or of a phosphorus-containing acid, or is a trivalent silyl radical,

R, if m is 4, is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid;

p is 1, 2 or 3,

R_1 is C_1-C_{12}alkyl, C_5-C_7cycloalkyl, C_7-C_8aralkyl, C_2-C_{18}alkanoyl, C_3-C_5alkenoyl or benzoyl;

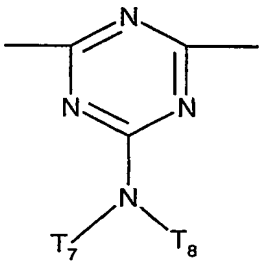
when p is 1,

R_2 is C_1-C_{18}alkyl, C_5-C_7cycloalkyl, C_2-C_8alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula -$CH_2CH(OH)$-Z or of the formula -CO-Z- or -CONH-Z wherein Z is hydrogen, methyl or phenyl; or

when p is 2,

R_2 is C_2-C_{12}alkylene, C_6-C_{12}-arylene, xylylene, a -$CH_2CH(OH)CH_2$-O-B-O-$CH_2CH(OH)CH_2$- group, wherein B is C_2-C_{10}alkylene, C_6-C_{15}arylene or C_6-C_{12}cycloalkylene; or, provided that R_1 is not alkanoyl, alkenoyl or benzoyl, R_2 can also be a divalent acyl radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid, or can be the group -CO-; or R_1 and R_2 together when p is 1 can be the cyclic acyl radical of an aliphatic or aromatic 1,2- or 1,3-dicarboxylic acid; or

R_2 is a group



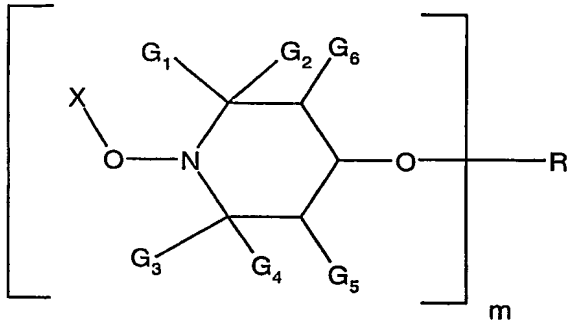
where T_7 and T_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms, or T_7 and T_8 together are alkylene of 4 to 6 carbon atoms or 3-oxapentamethylene;

when p is 3,

R_2 is 2,4,6-triazinyl; and

X is as defined in claim 5.

8. A process according to claim 7 wherein component a1) and a2) are of formula A, A', B, B' or O, O'



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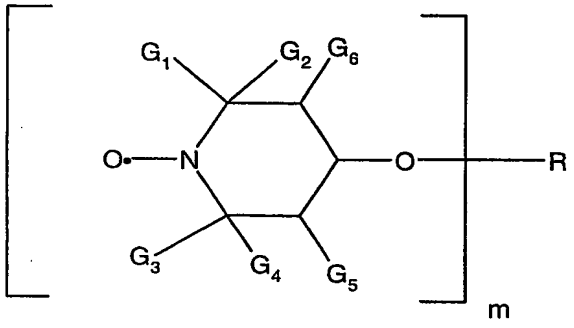
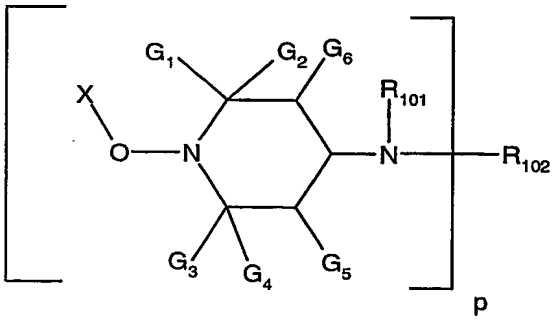


(A')



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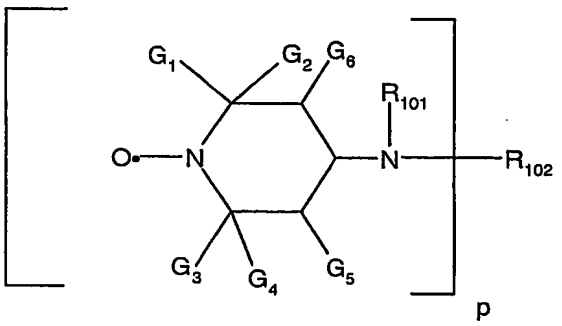

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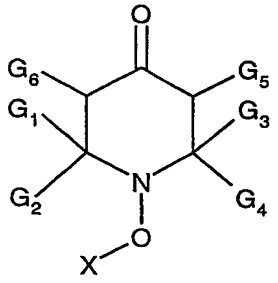

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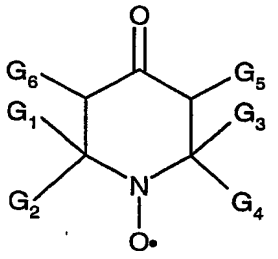

(O') ,

wherein

m is 1,

R is hydrogen, C_1-C_{18}alkyl which is uninterrupted or interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

p is 1;

R_{101} is C_1-C_{12}alkyl, C_5-C_7cycloalkyl, C_7-C_8aralkyl, C_2-C_{18}alkanoyl, C_3-C_5alkenoyl or benzoyl;

R_{102} is C_1-C_{18}alkyl, C_5-C_7cycloalkyl, C_2-C_8alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula $-CH_2CH(OH)-Z$ or of the formula -CO-Z or -CONH-Z wherein Z is hydrogen, methyl or phenyl;

G_6 is hydrogen and G_5 is hydrogen or C_1-C_4alkyl,

G_1, G_2, G_3 and G_4 are methyl; or

G_1 and G_3 are methyl and G_2 and G_4 are ethyl or propyl or G_1 and G_2 are methyl and G_3 and G_4 are ethyl or propyl; and

X is selected from the group consisting of

$-CH_2$-phenyl, CH_3CH-phenyl, $(CH_3)_2C$-phenyl, $(C_5$-C_6cycloalkyl$)_2CCN$, $(CH_3)_2CCN$, $-CH_2CH=CH_2$, $CH_3CH-CH=CH_2$ $(C_1$-C_4alkyl$)CR_{20}$-C(O)-phenyl, $(C_1$-$C_4)$alkyl-CR_{20}-C(O)-$(C_1$-

C_4)alkoxy, (C_1-C_4)alkyl-CR_{20}-C(O)-(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-N-di(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-NH(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-NH_2, wherein
R_{20} is hydrogen or (C_1-C_4)alkyl.

9. A process according to claim 7 wherein G_2 and G_4 are ethyl, G_1 and G_3 are methyl, G_6 is hydrogen and G_5 is methyl.

10. A process according to claim 1 wherein the free radical initiator of component a2) is a bis-azo compound, a peroxide, a perester or a hydroperoxide.

11. A process according to claim 1, wherein the nitroxylether of component a1) or the nitroxyl radical of component a2) is present in an amount of from 0.001 mol-% to 20 mol-%, based on the monomer or monomer mixture.

12. A process according to claim 1, wherein the free radical initiator is present in an amount of from 0.001 mol-% to 20 mol-%, based on the monomer or monomer mixture.

13. A process according to claim 1, wherein the ethylenically unsaturated monomer is selected from the group consisting of styrene, substituted styrene, conjugated dienes, vinyl acetate, vinylpyrrolidone, vinylimidazole, maleic anhydride, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles, (alkyl)acrylamides, vinyl halides or vinylidene halides.

14. A process according to claim 12, wherein the ethylenically unsaturated monomer is a compound of formula $CH_2=C(R_a)-(C=Z)-R_b$, wherein R_a is hydrogen or C_1-C_4alkyl, R_b is NH_2, $O^-(Me^+)$, glycidyl, unsubstituted C_1-C_{18}alkoxy, C_2-C_{100}alkoxy interrupted by at least one N and/or O atom, or hydroxy-substituted C_1-C_{18}alkoxy, unsubstituted C_1-C_{18}alkylamino, di(C_1-C_{18}alkyl)amino, hydroxy-substituted C_1-C_{18}alkylamino or hydroxy-substituted di(C_1-C_{18}alkyl)amino, -O-CH_2-CH_2-$N(CH_3)_2$ or -O-CH_2-CH_2-$N^+H(CH_3)_2$ An^-;
An^- is a anion of a monovalent organic or inorganic acid;
Me is a monovalent metal atom or the ammonium ion.
Z is oxygen or sulfur.

15. A process according to claim 1 wherein step B) is performed in an extruder, mixer or kneading apparatus.

16. A process according to claim 1 wherein in step B) additionally a processing stabilizer and/or antioxidant is added.

17. A process according to claim 1 wherein in step B) additionally a radical generator is added.

18. A process according to claim 1 wherein the nitroxyl terminated polymer or oligomer of step A) has an average molecular weight of from 1000 to 100 000 Dalton.

19. A process according to claim 1 wherein the nitroxyl terminated polymer or oligomer of step A) has a polydispersity PD from 1.0 to 2.0.

20. A process according to claim 1 wherein the nitroxyl terminated polymer or oligomer of step A) is added to the thermoplastic or elastomeric polymer or copolymer in an amount from 0.1% to 50% by weight based on the weight of the thermoplastic or elastomeric polymer or copolymer.

21. A grafted thermoplastic or elastomeric polymer or copolymer obtained according to claim 1.

22. Use of a nitroxyl terminated polymer or oligomer for the preparation of a grafted thermoplastic or elastomeric polymer or copolymer comprising heating mixing and reacting the nitroxyl terminated oligomer or polymer together with a thermoplastic or elastic polymer or copolymer at a temperature of between 120° C and 300° C.